Formulating for Improved Flexibility and Impact Resistance

Chuck Danick
Danick Specialties & Support Inc.
1390 Windward Lane
Niceville FL 32578

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Abstract:

Formulating powder coatings for improved flexibility and impact resistance can be accomplished a number of ways.

• Selecting the resin system

• Optimizing adhesion of the powder coating

• Assuring full cure of the powder coating

• Including additives in the powder coating

• Modifying or adding an additional curative

• Reducing filler content

• Using thinner films

Most recently, powder coating manufacturers have been seeking approaches to improve the flexibility and impact resistance of "super-durable" powder coatings.
This paper will cover the various strategies used to improve flexibility and improve impact resistance of powder coatings.

All powder coatings are based upon resin systems that contribute to the ultimate performance capabilities of each powder coating.

When powder coatings are subjected to conditions beyond these performance capabilities, the powder coatings fail. 3.0
Powder coating TDS, technical data sheets, should describe flexibility as a minimum diameter bend that is easily passed at a given film thickness.

In addition to the powder coating properties, there are other parameters in the coating system that can reduce coating performance when bending or post forming.

For powder coatings to have good impact and flexibility, the powder coating must have good adhesion properties.

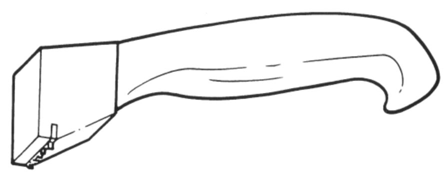
Adhesion – Without good powder coating adhesion, the coating disbonds from the substrate leaving the substrate unprotected from corrosion.
Poor adhesion leads to poor flexibility. Flexibility is directly proportional to adhesion.
Good adhesion requires that the coating material be brought into intimate contact with the surface or a firmly bonded chemical pretreatment layer. Proper pretreatment is essential for good corrosion resistance of powder coatings.3.0
In the case of thermosetting powder coatings, most of the coating properties are determined by the binder which is comprised of the powder coating resin and the curing agent. There is probably no other type of coating where the resin and coating chemists are forced to make so many compromises. 1.0

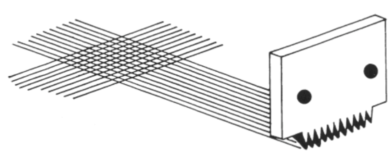
Cure – Flexibility is definitely reduced when the powder has not been properly cured. Even though powder coatings are very robust to variations in production oven cure conditions, when they are cured below or beyond the proper range, difficulties with performance properties will start.
Under cure results from shortened oven time, reduced temperature or heavy parts that heat up more slowly. 3.0
Over cure occurs with extended oven time, higher temperature or lightweight parts that heat up fast.
An indication of under cure would be open cracks, or even shattering, when test panels are bent.
The powder supplier can suggest modifications or alternatives that will work within the system performance parameters.
Moving to greater physical performance can involve compromise in other properties. If the coating is reduced gloss or textured, a change in appearance may be necessary for greater flexibility. Changes in specific gravity or basic coating chemistry may also occur when improving flexibility.
To minimize coating formulation changes, consider what can be done on the coating line to improve results, and consider what performance properties or appearance properties of the powder coating may be negotiable if a material change is expected.

Film thickness – The coating flexibility will change inversely to film thickness.3.0 In other words, flexibility decreases as film thickness increases. Maintain control of film thickness, especially on parts destined for post forming.

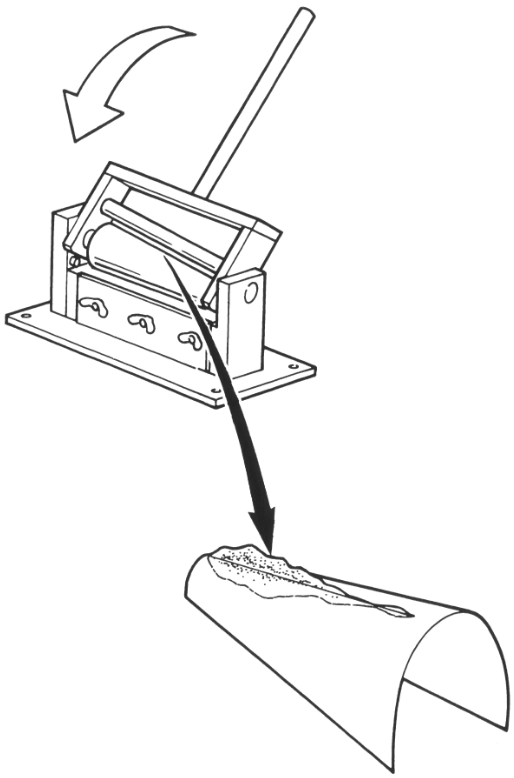
Testing flexibility – The common test for flexibility on bend diameters from 1/8 inch to 1.5 inches is ASTM D522: Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings. For even tighter bends, the T-bend method is found in ASTM D 4145: Standard Test Method for Coating Flexibility of Pre-painted Sheet.

Cross Hatch Adhesion 7.0





Conical Mandrel Flexibility



Conical Mandrel Results:

The red panel shows a failure at 1/8-3/16 inch conical mandrel

Formulating powder coatings for improved flexibility and impact resistance can be accomplished via multiple approaches:

- **Selection of resin system**

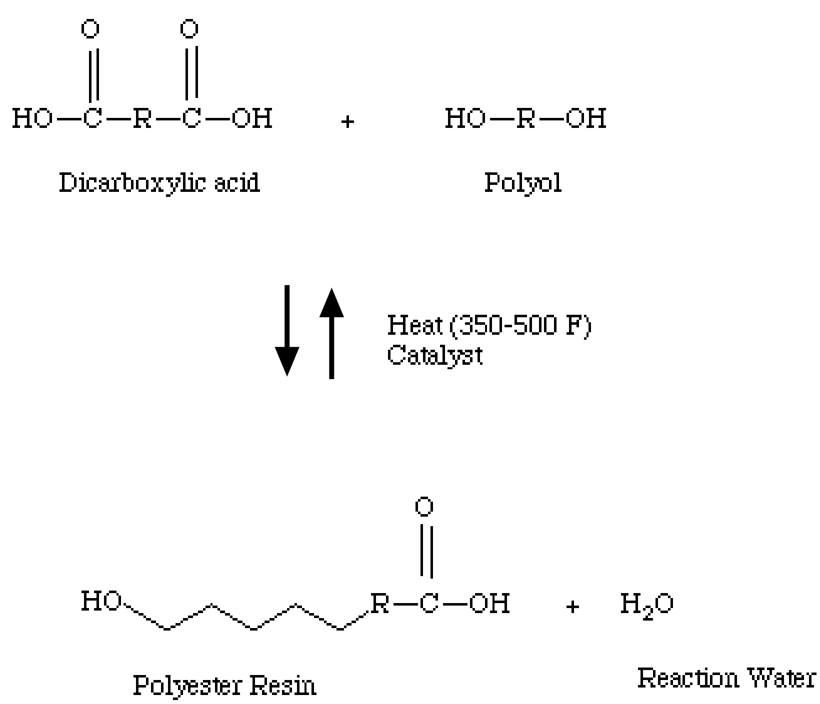
Polyester Resins as Binders for Powder Coatings
Most polyester resins used for the thin film decorative powder coating market today are thermosetting polyesters. Thermosetting polyesters can be defined as typically having functional groups such as hydroxyl, OH or carboxyl, COOH functionality. Hydroxyl functional polyesters react with curatives such as polymeric blocked isocyanates to form a film that melts, flows, and chemically reacts only once. Thermoplastic polyesters are not designed to chemically react during the application process when the coating is subjected to heat causing the coating to melt and flow. The final physical properties of thermoplastic resins are determined by their structural components and molecular weight of the resin; where as the final physical properties of thermosetting resins are determined by the combination of the thermosetting resin and the

curative chosen. Thermosetting resins can be formulated to achieve higher flows and thinner films than thermoplastic resins. Thermosetting resins usually have high flows at lower bake temperatures than their thermoplastic counter parts.

Polyester Synthesis: 4.0

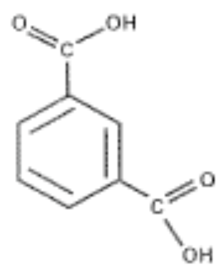
The most widely used reactants are **neopentyl glycol** and **terephthalic acid**. Numerous other difunctional acids and glycols are used to impart particular properties to the coating, such as increased detergent resistance or improved flexibility. These polyesters can be designed to possess two or more hydroxyl groups per molecule, (hydroxyl functional) or two or more carboxyl groups per molecule (carboxyl functional or acid functional)..

The polyesters which are useful for low temperature cure with epoxides like TGIC are thermosetting carboxyl types with a sufficiently high enough Tg, glass transition temperature, of at least 45-50 C. Both the Tg and melt viscosity of the polyester are greatly influenced by the choice of monomers. More UV durable products are attained as the level of isophthalic acid is increased. Impact resistance must be optimized as the level of isophthalic acid is increased.

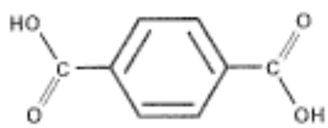


Reactants used in formulating thermosetting polyester powder resins:

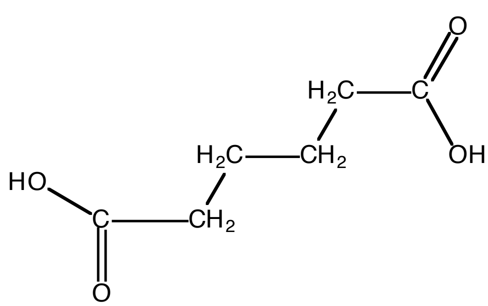
Isophthalic Acid is used for formulating "super-durable" polyesters



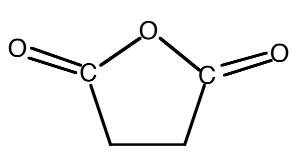
Terephthalic Acid is used for formulating standard durability polyesters



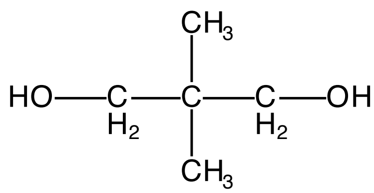
Adipic Acid



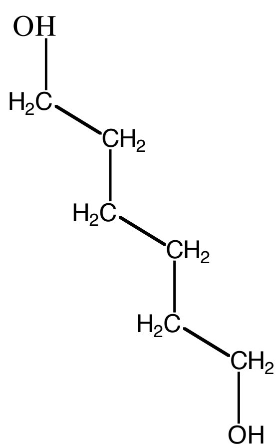
Succinic Anhydride



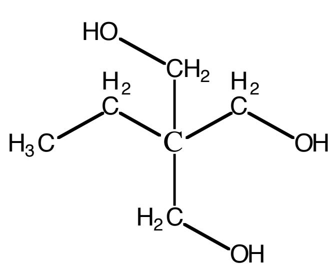
Neopentyl Glycol



1,6 Hexane diol

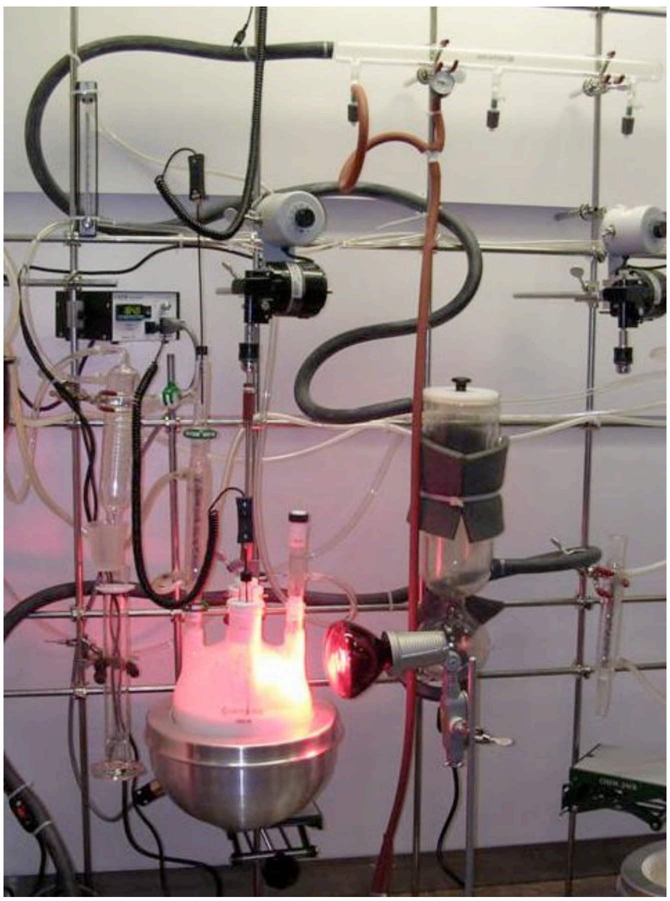


Trimethylol propane



Polyester Synthesis Apparatus:

The laboratory apparatus pictured below can be used to synthesize polyester resins for powder coatings.



The resulting lab resin is discharged in molten form. It is then cooled and crushed to prepare it for use in a typical thermosetting polyester powder coating formulation.

A typical thermosetting polyester powder coating will contain: polyester resin with carboxyl or hydroxyl functionality, a curative for the chosen resin, flow control additive, degassing additive, pigments, fillers and other potential additives.

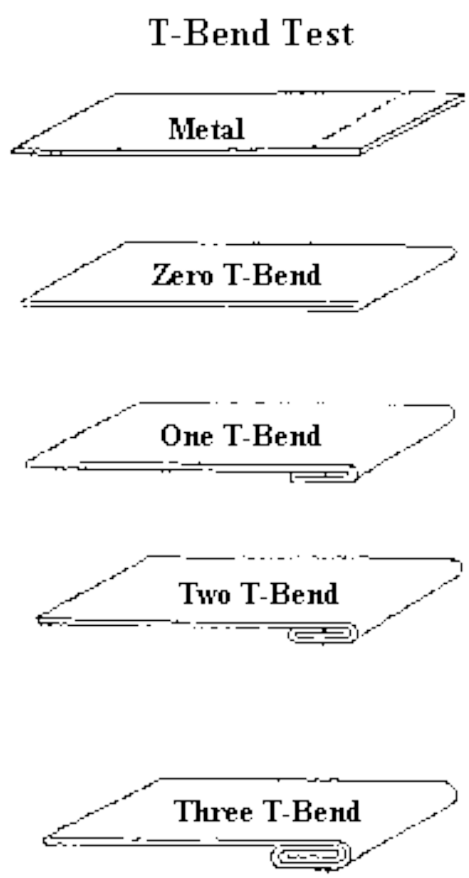
Polyester Resin:

Polyester resins are generally cooled and flaked to allow easy weighing, premixing, compounding etc.

Polyester resins which are recognized as having superior flexibility are being marketed. Use of these polyesters will result in powder coatings with better flexibility.
Some products are being promoted for zero T-bend applications.
What is 0-T? (See T-Bend Test diagram)
When you think of 0-T applications, coil coatings and blank coatings come to mind.
These resins typically have been modified during formulation/manufacture.

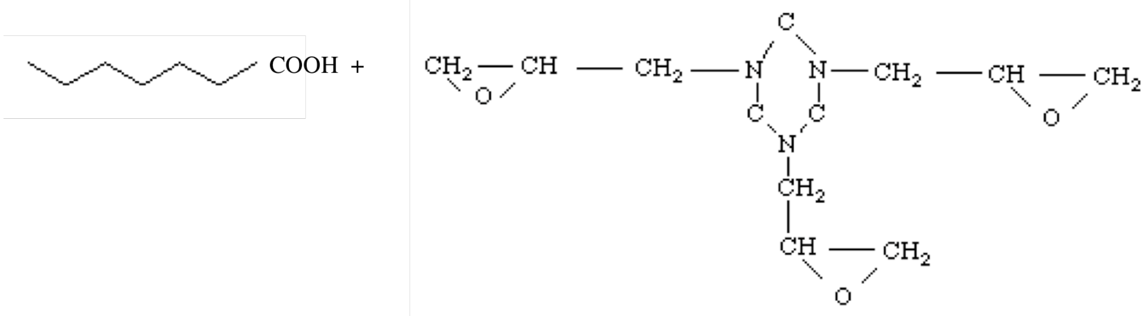
Polyesters for powder coatings are comprised of dicarboxylic acids and diols . They can be modified for appearance and performance properties with tri functional carboxylic acids/anhydrides and tri functional polyols. The basic approach has been replacement of some of the Dicarboxylic acid, Terephthalic acid or Isophthalic acid with flexibilizing reactants such as Adipic acid or 1,6 Hexane diol, for example.

The challenge with any formulation is to balance the properties so that when flexibility is increased, other resin parameters such as glass transition temperature Tg, do not decrease too much.
The typical Tg range of standard thermosetting polyesters for powder coatings is 50-60 degrees C.
Resins with lower Tg’s can contribute to sintering ,clumping of the powder coating.

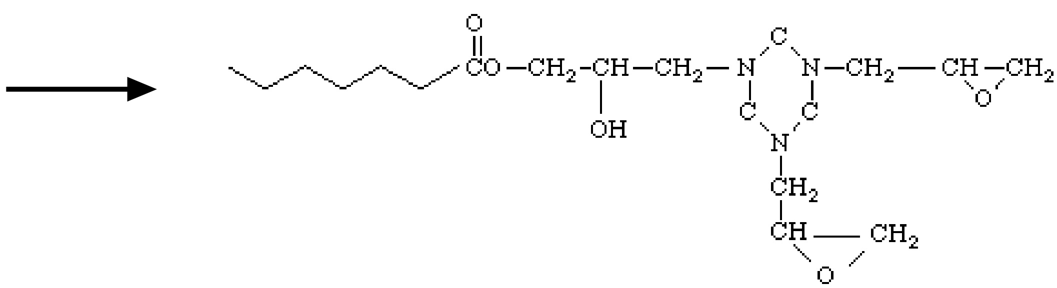


Carboxyl polyesters cured with TGIC

Most conventional TGIC cured polyesters are linear carboxyl polyesters. When they are baked 10-15 minutes at 160-180 C (320-360 F), these products can give excellent powder coatings. The lower temperature cure of these powder coatings is achieved by incorporating a catalyst into the polyester. The chemical reaction involved is condensation of a carboxylic group from the polyester with the oxirane functionality of the TGIC.



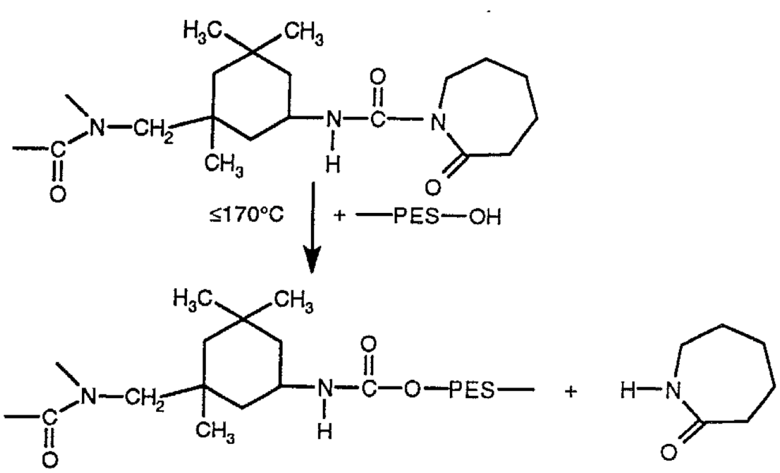
Polyester Resin Triglycidyl isocyanurate (TGIC)



Hydroxyl functional polyester cured with a blocked isocyanate

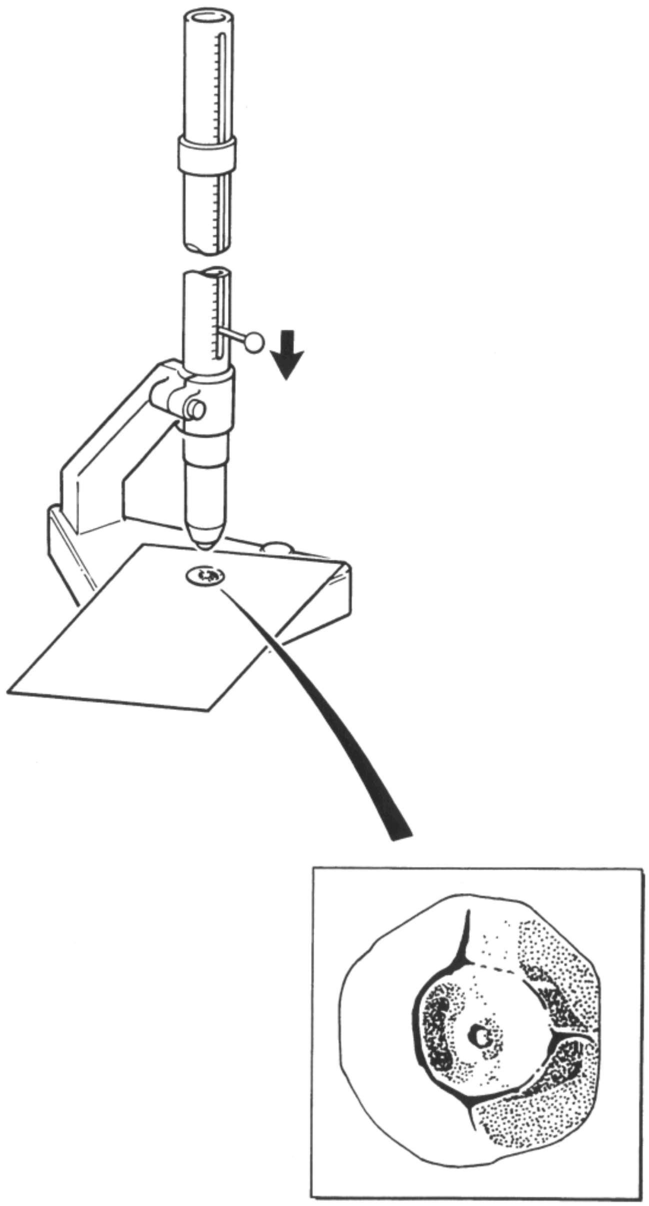
The North American market has been dominated by this urethane chemistry for over 20 years. Most recently, due to lower costs of competitive chemistries such as TGIC, urethane systems have lost market share.
Polyester-urethanes provide advantages to the powder coatings formulator. Polyester-urethanes can be described as achieving the ideal attributes of a thermosetting coating; namely to be a highly reactive system during cure conditions and to be virtually unreactive during manufacture, storage and application. These ideals are achieved by the ring opening reaction associated with uretdione curing agents used with hydroxyl terminated polyesters or through the use of polymeric blocked isocyanate
curing agents.

Polymeric blocked isocyanate curative reacting with a hydroxyl polyester, PES-OH.



During the curing reaction, the blocking agent, such as E-caprolactam evolves

Impact Resistance Test : (ASTM 2794) 7.0

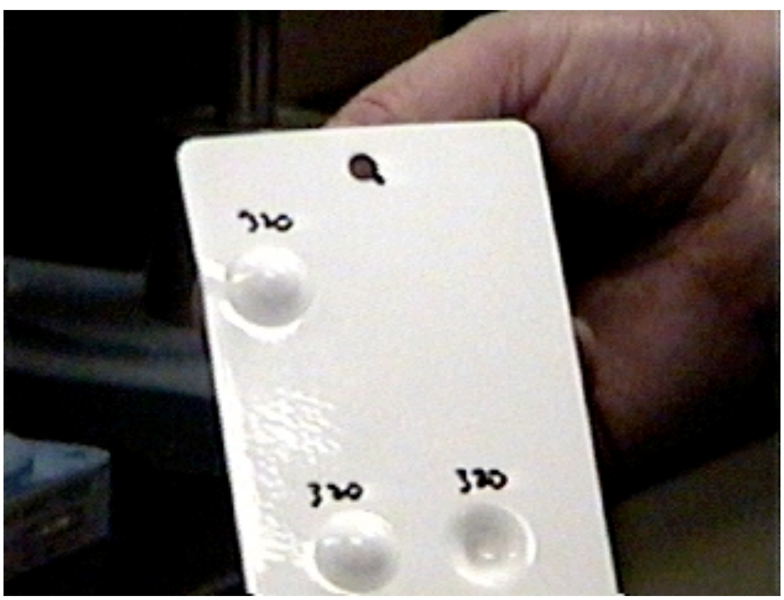


The target for thermosetting powder resins Tg is approximately 50-60 C. This target maintains resistance to powder coating sintering and clumping under most use conditions.
Polyester powder resins that have been modified for increased flexibility may have slightly lower Tg's, typically in the range of 50-55 C.

Another reactant , such as Succinic anhydride for example, has been used to improve flow and flexibility of thermosetting hydroxyl polyesters. This concept is covered in a US patent. 10.0

Linear polyesters have been shown to have better flexibility and flow than some of the more highly branched products. Increased branching can help increase toughness of the powder coating resulting in improved impact resistance, especially when molecular weight of the resin is increased.
The down side is that flow may be decreased. We have to always consider balancing of the conflicting performance parameters.

This is an example of a toughened product resulting from increased branching and higher molecular weight.

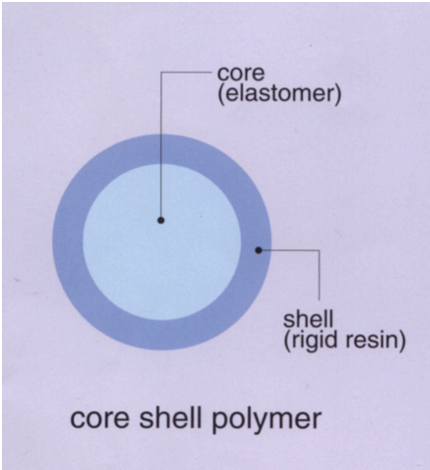


• **Additives to improve flexibility/impact** 5.0

Additives allow the powder coatings formulator to have more control over the final powder coating performance characteristics.
Surfactants (Wetting Agents) are one class of additives.
Surfactants promote pigment and filler wetting while improving flow and leveling of the powder coating. In addition, they promote substrate wet-out (during cure) which improves adhesion and therefore corrosion resistance. They often increase gloss and DOI (distinctness of image) of the cured film as well. Surfactant levels can range from 0.1% to about 0.5% active substance on total formula.

Other additives such as micro spheres that are comprised of a hard shell with a soft core have been shown to increase the impact resistance of "super-durable" powder coatings from less than 20 inch-lbs to 160/160 inch-lbs.

Super-durable polyester 6.0	**58.74**
TGIC	**4.37**
Flow agent	**1.05**
Benzoin	**0.39**
Core shell Additive	**2.91**
TiO2	**32.54**
	100.00



• Modifying or adding additional curing agent

Another route to improved flexibility of powder coatings is to use curatives that enhance flexibility and impact resistance.
For example, hydroxyl functional polyesters can be cured with polymeric blocked isocyanate curatives that will enhance flexibility/impact.. The more linear curatives have been shown to enhance powder coating flexibility.
Super-durable TGIC cured polyesters have improved impact resistance and flexibility when 5-7% urethane curative is added to the powder coating formulation

Super-durable polyester 6.0	**53.95**
TGIC	**4.17**
Flow agent	**1.62**
Benzoin	**0.47**
Uretdione curative	**5.20**
TiO2	**34.60**
	100.00

The above formulation has achieved 60-100 in-lbs impact resistance.

• **Reducing pigment/filler content** 9.0

General Information:
Fillers are the lowest cost component used in powder coatings, they reduce the raw material cost of the formulated products. Fillers can improve film hardness, enhance corrosion resistance, increase hiding, catalyze cure, reduce gloss, or assist in creating textured finishes. Unfortunately, fillers increase the specific gravity in coating powders which reduces the coverage. (square feet per pound at a given film thickness). Formulators have to balance formulated raw material cost and specific gravity of their products under development to obtain 'the biggest bang for the buck', i.e. the lowest possible cost of applied powder per square foot.
Typically, a clear powder coating, using defined cure chemistry, will have the optimum flexibility and impact resistance. As fillers and pigments are added, flexibility and impact resistance will eventually decrease.

Flexible polyester 6.0	**62.50**	
TGIC	**4.70**	
Flow Agent	**1.20**	
Benzoin	**0.50**	
Antioxidant	**0.15**	
TiO2	**30.95**	
	100.00	This formulation has achieved 0-T bend .

Applications for increased flexibility powder coatings

Increased flexibility powder coatings allow applications such as blank coating.

Blank coating involves applying a uniform powder coating at high production rates on flat sheets, or blanks, before the metal is formed. Blanks can be stamped or sheared, with all cutouts, holes, and notches punched to final dimensions before parts are formed. Then, the blanks can be pretreated, powder-coated, cured, and finally formed into 3-D parts.

Some of the benefits of powder coating blanks include 8.0:

1. High production rates
2. Low operating costs (energy, labor, chemicals, water, powder, and wastewater)
3. Precise and uniform film buildup
4. Low floor space requirements
5. High levels of automation
6. Simplified work-in-process (WIP)
7. High-quality finishes
8. Reduced hazardous waste

Blank coating is being considered for other industrial applications in addition to the appliance industry:
These include:

1. Lighting fixtures
2. Metal furniture
3. Automotive components
4. Water heaters
5. Shelving, racking, and displays
6. Air conditioners
7. Home furnaces
8. Modular building components

Powder coatings can be formulated to meet these challenges.

Using thin films: 7.0

Flexibility is increased as the film thickness is decreased.
Some thermoset polyester powder coatings achieve 0-T bend flexibility when applied at 25 microns
(One mil) but only pass 1/8-inch mandrel flex at 2-3 mils (50-75 microns)

Conclusions:

Formulating powder coatings for increased flexibility can help expand the markets suitable for powder coatings.

Formulating powder coatings for increased flexibility and impact resistance can be achieved via multiple approaches.

The most stringent flexibility performance such as 0-T bend requires specific resins designed for this property.

The pathway to increased flexibility and impact resistance is now well defined.

Typical Powder Coating Tests 7.0

	Test Methods	Standards
•	Film thickness	ISO 2808; B.S. 3900D5
•	Gloss	ISO 2813; ASTM D523; DIN 67530
•	Flow (orange-peel)	
•	Color: Visual	ISO 3668
•	Colorimetry	ISO 7724
•	Adhesion (cross-cut test)	ISO 2409; ASTM D3002
•	Impact resistance	ISO 6272; ASTM D2794
•	Cylindrical mandrel bend test	ISO 1519; ASTM D1737; DIN 53152; NFT 30040
	Conical mandrel bend test	ISO 6860; ASTM D552; NFT 30078
•	Persoz pendulum hardness	ISO 1552; NFT 30016
•	König pendulum hardness	ISO 3711; DIN 53157
•	Buchholz indentation hardness	ISO 2815; DIN 53153
•	Scratch resistance	ISO 1518; ASTM 2793
•	Erichesen cupping test	ISO 1520; DIN 50102; B.S. 3900; NFT 30019
•	Pencil hardness	ASTM D3363
•	Taber abrasion resistance	ASTM D821; DIN 53774; ANF T 30015
•	Heat resistance	- - - - - - - - - -
•	Humidity resistance test	ISO 6270; DIN 50017; B.S. 3900 F2
•	Kesternich sulphur test	ISO 3231; DIN 50018; B.S. 3900 F8
•	Salt spray test	ISO 9227; DIN 50021;
	Acetic acid salt spray test	ISO 3769; B.S. 6496 C15
•	Mortar resistance	ASTM C207; B.S. 6496 C15
•	Chemical resistance	- - - - - - - - - - - -
•	Detergent resistance	- - - - - - - -- - - --

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Dicarboxy acid Trimellitate Thermosetting Resin
Inventors: Charles Danick and K.A. Pai Panandiker

Biographical Data:

His educational background includes Purdue University, and some graduate polymer science courses at Roosevelt University, Chicago, IL.
After working for a variety of major corporations for close to 30 years, Chuck has taken the knowledge he has amassed to start his own business.
Danick Specialties & Support Inc. was officially incorporated February 5, 2003.
Chuck is well known for his dedication to advancing the powder coating industry.
He is currently a member of the Powder Coating Institute, via ***Danick Specialties & Support, Inc.***
He has served the PCI, in the past, as Chairperson of the Health and Safety Subcommitte for 5 years.
Chuck acquired the combination of polymer synthesis/formulation skills with powder coating formulation and research management skills during his career. This is a unique combination, that provides value to the coatings industry.